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Four Coordinate Complexes of Carbon

by

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Prepared for publication

(In condensed form)

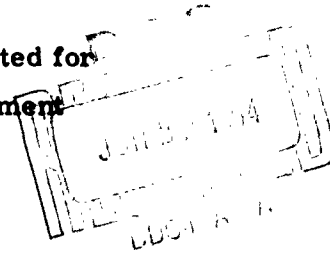
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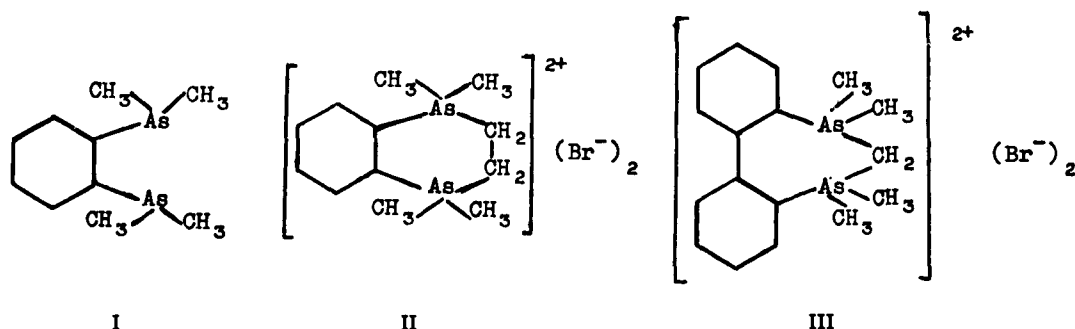
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## FOUR COORDINATE COMPLEXES OF CARBON

### 1. INTRODUCTION

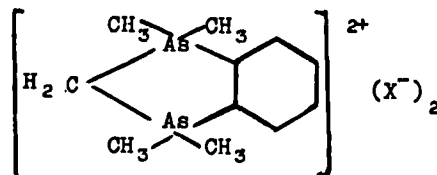
Studies in these laboratories of complexes formed by the  $1s^2$  core (light) elements, beryllium and boron, with the ditertiary arsine, o-phenylene bis(dimethyl arsine) <sup>1,2</sup> (I) have now been extended to carbon.

Compounds of the type  $[\text{CH}_3\text{AsR}_3]^+ \text{X}^-$  have been known for a long time and more recently <sup>3</sup> derivatives of the type II and III have also been described.



We have now developed this series to include complexes in which the same carbon is coordinated to two, three and four arsenic atoms; examples of the last two of these were previously unknown.

### 2. Di hydro (o-phenylenebisdimethyl arsine) carbon IV salts



#### Preparation:

(a) Bromide. Equimolar quantities of o-phenylene bisdimethyl arsine and dibromomethane were reacted and the yellow solid, on recrystallisation from methanol gave white crystals M. P. 220°.

Found C, 28.5, H, 4.3; As, 32.4; Br, 35.3%

$\text{C}_{11}\text{H}_{12}\text{As}_2\text{Br}_2$  requires C, 28.8; H, 3.9; As, 32.5; Br, 34.8%

Equivalent conductivity of  $10^{-3}\text{M}$  aqueous solution = 250 mhos

(b) The iodide, M. P. 239° was prepared in an analogous way using diiodomethane.

Found C, 23.7; H, 2.9; I, 45.8%

$C_{11}H_{12}As_2I_2$  requires C, 23.8; H, 3.2; I, 45.8%

Equivalent conductivity of  $10^{-3}M$  aqueous solution = 246 mhos

(c) The perchlorate was prepared by adding a hot saturated ethanolic solution of sodium perchlorate to a hot saturated ethanolic solution of the bromide. The perchlorate crystallised out on cooling as shiny white needles, M. P. 270°.

Found C, 26.7; H, 3.6; As, 30.0%

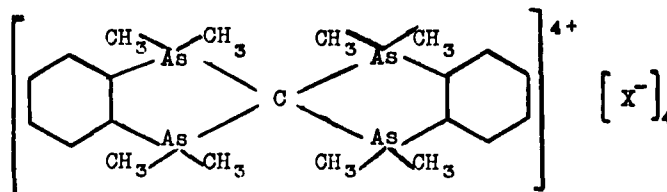
Calc. for  $C_{11}H_{12}O_8As_2Cl_2$  C, 26.4; H, 3.6; As, 30.0%

Equivalent conductivity of  $10^{-3}M$  aqueous solution = 202 mhos

PROPERTIES These complexes are stable white crystalline salts readily soluble in water and the halide ions are freely titrateable with silver nitrate. The conductivities correspond closely the values expected for 2 : 1 electrolytes.

It is possible to evaporate the aqueous solution and recover the complex unchanged.

### 3. bis (o-phenylenebisdimethyl arsine) carbon (IV) salts



#### Preparation:

The Bromide was obtained by reaction two moles of the diarsine with one mole of carbon tetrabromide. The solid reaction product was recrystallised from absolute ethanol/ether and the bromide obtained as white crystals M. P. 82°.

Found C, 28.0; H, 3.3; As, 30.0; Br, 35.6%

Calc. for  $C_{21}H_{32}As_4Br_4$  C, 28.0; H, 3.6; As, 33.2; Br, 35.4%

The iodide was obtained in a similar way but using carbon tetraiodide and obtained as white crystals M. P. 231°.

Found C, 23.2; H, 2.9; As, 27.1; I, 46.9%

$C_{21}H_{32}As_4I_4$  requires C, 23.1; H, 3.0; As, 27.4; I, 46.5%

The perchlorate was prepared by mixing hot ethanolic solutions of the bromide and sodium perchlorate and crystallised out on cooling. M.P. 243°.

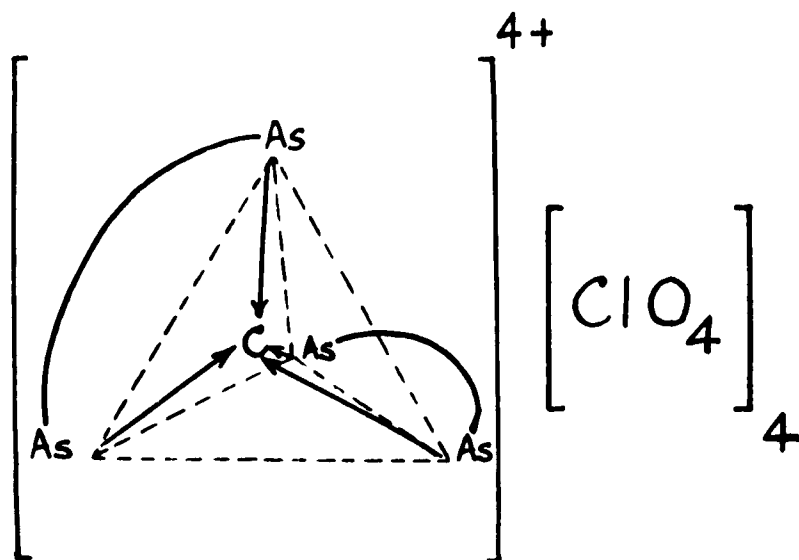
Found C, 26.3; H, 4.0; As, 30.7%

$C_{21}H_{32}O_{16}As_4Cl_4$  requires C, 25.7; H, 3.3; As, 30.5%

**PROPERTIES** These complexes are stable white crystalline solids that are extremely soluble in water. The bromide and iodide ions are readily titrateable and the conductivities indicate extensive ion association which is not unusual for ions bearing this high positive charge.

The low melting point of the bromide is of interest. It has been observed that, if the liquid is heated above 100° it appears to bubble and then resolidifies. The white solid formed does not remelt until the temperature is above 200°. The nature of this reaction is uncertain but similar degradations of quaternary arsonium halides, whereby methyl halide is evolved and the tertiary arsine formed are not uncommon. The infra-red spectra have been recorded.

**4. DISCUSSION** The unique feature of these new compounds is the number of quaternary arsenic atoms (or coordinate links) associated with the same carbon atom. Just as one can formulate complexes of metallic elements with four coordinate links e.g. the complex  $[Zn(diamsine)_2](ClO_4)_2$  so the carbon compound can be written formally as shown in the figure. It is not suggested that there is any real distinction between the representation



Bis-o-phenylenebisdimethylarsine-carbon( $\overline{IV}$ )  
tetra-perchlorate.

$R_3As^+ \text{---} C \rightleftharpoons$  and  $R_3As \rightarrow \overset{+}{C} \rightleftharpoons$  but it is important to emphasise that no sharp distinction can be made between, say, Be(II) and C(IV) and that there is simply a gradual transition from Li(I) to C(IV) as the formal charge on the central atom increases.

We are now studying the reactions between  $CHBr_3$ ,  $CHI_3$ ,  $CBr_4$  and  $Cl_4$  with a variety of tri and quadridentate arsine ligands, both with aliphatic and aromatic skeletons.

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